“Energy Storage Applications Of Spinel and or Perovskite Nanostructures”

Synopsis in Candidature for the Degree of

Doctor of Philosophy in Physics

Submitted by

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1) Introduction

With the ever-increasing adaption of large-scale energy storage systems and electric devices, the energy storage capability of batteries and supercapacitors has faced increased demand and challenges. The electrodes of these devices have experienced radical change with the introduction of nano-scale materials. Novel materials consisting have attracted increasing attention due to their unique interfaces, robust architectures, and synergistic effect, and thus, ability to enhance the energy/power outputs as well as the lifespan of batteries [1]. Over the last decade, there has been a growing interest in the development of new high-performance electrodes and electrolytes for advanced energy storage systems. These systems are mostly batteries and supercapacitors that provide high energy, fast charge-discharge, and long cyclic endurance. Among other energy storage systems, supercapacitors, also known as electrochemical capacitors, stand out for their high power densities, fast charge-discharge rates, and excellent stability. In addition, low internal resistance, low weight, easy packaging, and broad operating temperature (0–70 °C) make them highly efficient devices for operational applications. The electrolyte plays an important role in electrochemical energy storage, providing ions as energy to systems. Different types of electrolyte systems such as liquid electrolytes, polymer electrolytes, and hydrogel electrolytes are commonly used in supercapacitor assemblies[2][3].

Since the decade, because of novel magnetic properties with reduced dimensions, a myriad of research activities in the synthesis and characterization of ferrite nanostructures have been undertaken as far as materials science and engineering technology are concerned. Spinel ferrite (MFe_2O_4 where 'M' is transition metal) nanostructures have been widely explored in literature for various applications including high-density magnetic recording, ferrofluid technology, biomedical drug delivery [6], and magnetic resonance imaging. In manganese ferrite ($MnFe_2O_4$)O_2- cations form cubic structure i.e. Mn_2+ and Fe_3+ are in two crystallographic positions.10 Alternatively, spinel ferrite can also be written in (AII+)[B2III+]O_4 II− form, where AII+ and BIII+ are divalent and trivalent cations. They generally occupy tetrahedral (A) and octahedral [B] sites. When divalent cations occupy tetrahedral (A) sites it is considered as normal spinel structure while when they occupy octahedral [B] sites, an inverse spinel structure is dominant. In the normal spinel structure, the bivalent ions (Mn_2+ in $MnFe_2O_4$) are at the tetrahedral positions and the trivalent ions (Fe_3+ in $MnFe_2O_4$) are at octahedral positions whereas in inverse spinel structure, bivalent ions are at halfway of the B positions, and trivalent

ions are in the rest of the B positions. Ferrite with mixed spinel phase can be obtained at high temperatures (>900 ◦C) where 20% of the Mn_2+ ions migrate from A to B positions[4]. The spinels occur as natural minerals. A few examples of spinels with striking features include $MgAl_2O_4$, $FeAl_2O_4$, and Fe_3O_4. The spinel with the metal ion Fe_3+ present in the largest molar concentration is ferrite, which generally demonstrates ferrimagnetic properties. The structure and crystal chemistry of spinels have comprehensively been addressed in the literature. The unit cell of a spinel structure contains thirty-two closely packed oxygen atoms[5]. Spinel, an intriguing and adaptable mineral, has garnered considerable interest in contemporary times owing to its distinctive characteristics and extensive array of practical uses. The mineral in question is a compound of magnesium, aluminium, and oxygen, with the chemical formula $MgAl_2O_4$.Moreover, spinel exhibits exceptional thermal stability, characterised by a melting point that surpasses 2,000 degrees Celsius. This attribute renders it well-suited for applications in situations with elevated temperatures. In recent years, spinel has emerged as a promising alternative to conventional semiconductors in the realm of electronics. The material's large bandgap enables it to operate effectively at elevated temperatures while retaining exceptional electrical conductivity. Using spinel-based electronic devices has potential opportunities for operation in challenging environments or high-power scenarios. In summary, spinel is a mineral of exceptional nature, possessing notable characteristics that render it greatly coveted across diverse industrial sectors. The remarkable properties of this material, including its high hardness, thermal stability, optical transparency, and electrical conductivity, have facilitated its use in several fields such as optics, transparent armour, and electronics. As ongoing research and development endeavours persist in their exploration of spinel's potential, it is anticipated that this material will increasingly discover a wider range of uses, characterised by its diversity and innovation, in the foreseeable future[6]. Perovskites are now being extensively researched as useful materials. When the charge storage method of oxygen-anion intercalation was suggested, perovskites as an anode material for supercapacitors received a lot of interest. By reviewing earlier work on perovskite materials for supercapacitors, this study condensed the anion-intercalation mechanism and the variables that affect the electrochemical performance of electrodes[7]. The development of electrode materials with exceptional electrochemical performance is of utmost importance, as the specific capacitance and energy density of supercapacitors are intimately associated with the electrodes employed. Perovskite oxides have garnered significant interest as potential electrode materials for supercapacitors due to their distinctive structure, compositional versatility, and intrinsic presence of oxygen vacancies[8].

Literature review

Ameerah N. Alqarni et al. reported The fabricated supercapacitor device showed successful energy density retention at a high current without losing power density and cyclic stability. The device containing SFNP-based composite electrodes achieved a specific energy of 57.24 Wh kg^{-1} at a specific power of 7.900 W kg^{-1} with excellent cyclic stability of 10,000 cycles. The prototype device was successfully powered with RGB LED light. The low-cost production of materials and high electrochemical performance may pave the way for using these nanocomposites for highly stable energy storage devices[9].

Mohan Reddy Pallavolu et al. designed spinal copper-doped cobalt oxide (Cu-Co_3O_4) nano boxes decorated functionalized-carbon nanotubes (f-CNTs) as hybrid redox-type material and agriculture crop-waste derived mesoporous activated carbon as a capacitive-type electrode for high-performance hybrid supercapacitors. The hybrid electrodes exhibit a maximum specific capacity of 130.7 mAh g^{-1} at 0.5 A g^{-1} with 86.7 % capacitance retention over 10,000 cycles. The high voltage hybrid supercapacitor is further fabricated with Cu-Co_3O_4 @F-CNTs as battery-type and biomass-derived activated carbon as capacitive-type electrodes, which demonstrate a high energy density of 30.8 Wh kg^{-1} at 5972 W kg^{-1} power density[10].

Chen Zhang et al. reported Sol-gel to make a honeycomb-shaped $LaMnO_3$ supercapacitor. This method controls material morphology by using an as-prepared carbon spherical material as a template. Honeycomb LaMnO3 perovskites function better when the dry gel is calcined at 600 °C, according to experiments. In particular, honeycomb $LaMnO_3$ perovskites (535 F g^{-1}) have a higher specific capacitance than sol-gel perovskites (247 F g^{-1})[11].

Shyam K. Gore et al. 2015 effectively synthesized ferrites of $CoBixFe_2{-}xO_4$ with different values of 'x' ranging from 0.0 to 0.2. The synthesis process involved utilizing a sol-gel self-combustion approach, followed by air-annealing the samples at a temperature of 500 °C for a duration of 4 hours. The confirmation of the development of a face-cantered cubic spinel cobalt ferrite has been achieved through analysis of the XRD spectra. Additionally, it has been observed that the shape of the cobalt ferrite is influenced by the level of Bi3+ doping. The EDX results provide confirmation of the systematic increase in the level of Bi_3+ doping. The presence of ferrimagnetism in both doped and undoped $CoFe_2O_4$ ferrites is substantiated by the analysis of the Mossbauer spectra. The findings presented in this study provide supporting evidence for a positive alteration in the magnetic properties of $CoFe_2O_4$ with the introduction

of Bi_3+ at varying concentrations. Consequently, these ferrites exhibit promising prospects for utilization in magnetic recording and memory systems[12].

Manohar K. Zate, and others 2016 reported Structural, morphological and electrochemical supercapacitive properties of sprayed manganese ferrite thin film electrode. In this report, investigates the structural, morphological characteristics, and electrochemical supercapacitor electrode application of thin films of manganese ferrite ($MnFe_2O_4$). The films were formed onto glass and stainless-steel substrates using the chemical spray method. X-ray diffraction patterns and scanning electron microscopy measurements are employed to verify the spinel structure and nodule-type morphology of the $MnFe_2O_4$ film obtained. The specific capacitance values for the as-deposited ferrite electrode in 1 M KOH, NaOH, Na_2SO_3, and Na_2SO_4 aqueous solutions, obtained using cyclic-voltammetry plots at a scan rate of 5 mV s^{-1}, are 313, 295, 146.02, and 180.51 Fg^{-1}, respectively. The electrochemical impedance spectrum provides evidence for the presence of pseudocapacitance behaviour in $MnFe_2O_4$ film electrodes that have not undergone any additional processing[13].

3) Objectives of the study

The research work will be focus on the following objectives: -

(1) Synthesize and characterize Spinel and or Perovskite electrode materials.
(2) Synthesize and characterization of Spinel and or Perovskite-based nanostructures.
(3) Study of Structure characterization of Spinel and or Perovskite compounds by using XRD, SEM, TEM and Raman spectrometer techniques.
(4) Investigate the influence of Spinel and or Perovskite on the supercapacitor performances.
(5) Study the supercapacitor performance of the fabricated Spinel and or Perovskite electrodes.
(6) Compare these results with data reported previously & publish manuscript in international journal.
(7) Design thesis accordingly based on the data available.

4) Methods

Hydrothermal method.

It is important branches of inorganic synthesis. Hydrothermal technique is not just confined to the syntheses and growth of conventional and advanced materials but also take a very broad shape, covering several interdisciplinary branches of science and widely applied.

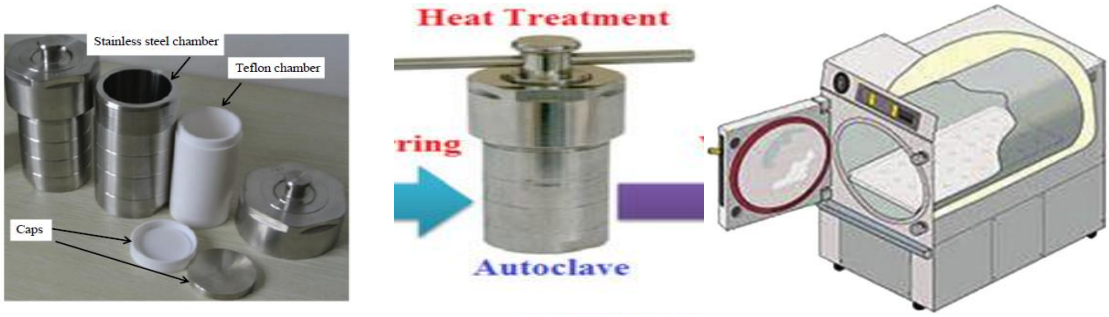

Fig 1: Diagram of hydrothermal method

Hydrothermal method for crystallizing substances from high-temperature aqueous solutions at high vapour pressures; also termed "hydrothermal method.'' The term "hydrothermal" is of geologic origin. Hydrothermal synthesis can be defined as a method of synthesis of single crystals that depends on the solubility of minerals in hot water under high pressure. The crystal growth is performed in an apparatus consisting of a steel pressure vessel called an autoclave in which a nutrient is supplied along with water. A temperature gradient is maintained between the opposite ends of the growth chamber. At the hotter end the nutrient solute dissolves, while at the cooler end it is deposited on a seed crystal, growing the desired crystal[14].

Chemical bath deposition[15][14][15][14].

(CBD) is a low-cost, low-temperature method for producing large-area semiconductor thin films (at temperatures ranging from 25 to 90 ℃). For the deposition of different nanometal chalcogenide thin films, (CBD) is routinely utilised. The regulated precipitation of the chemicals from the solution results in excellent deposits on appropriate surfaces. It does not require high-voltage equipment, can operate at room temperature (between 30 and 100 ℃) and is thus affordable. Only an aqueous solution containing a few common chemicals and a substrate for the film to be deposited are required for this deposition method. Transition metal oxide films were created by optimising CBD preparative factors such as deposition temperature, duration, pH, complexing agent, and so on. Various complexing techniques were used to deposit metal oxide films from a solution containing precursor[15].

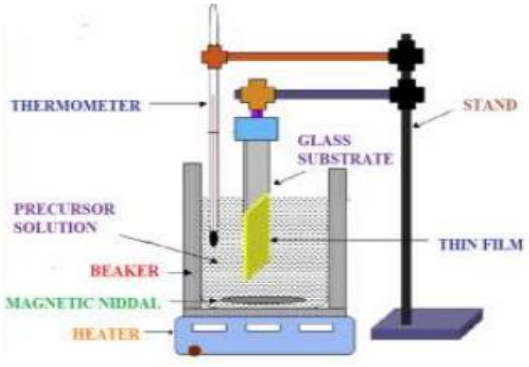

Fig 2: Diagram of chemical bath deposition method

SILAR Method.

The successive ionic layer adsorption and reaction (SILAR) approach is a simple, less expensive, and faster method for the deposition of binary semiconducting thin films. It can also be used for large-area thin film deposition. The process was used to grow a variety of II–VI compounds, including CdS, ZnS, and CdS/ZnS multilayers. The substrate is submerged separately in two precursor solutions and rinsed in between with water to remove loosely bound species in the SILAR process. one SILAR cycle consists of cation precursor adsorption, water rinsing, anion precursor adsorption, reaction, and another rinsing. The thin film's growth, on the other hand, can be precisely regulated to within one SILAR cycle[16].

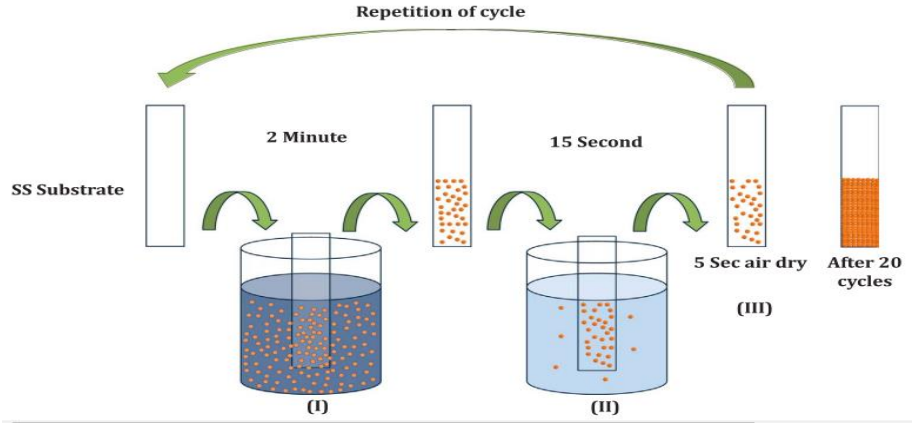

Fig 3: Steps involved in SILAR

Sol-gel method.

The sol-gel process is a more chemical method (wet chemical method) for the synthesis of various nanostructures, especially metal oxide nanoparticles. In this method, the molecular precursor (usually metal alkoxide) is dissolved in water or alcohol and converted to gel by heating and stirring by hydrolysis/alcoholises. Since the gel obtained from the hydrolysis/alcoholises process is wet or damp, it should be dried using appropriate methods depending on the desired properties and application of the gel. After the drying stage, the produced gels are powdered and then calcined. The sol-gel method is a cost-effective method and due to the low reaction temperature, there is good control over the chemical composition of the products. The sol-gel method is a conventional and industrial method for the synthesis of nanoparticles with different chemical compositions[17].

Characterization

Physical characterizations

a) Structural analysis

b) Surface morphology study.

c) Raman spectrometer

f) X-ray photoelectron spectroscopy (XPS)

Electrochemical measurement

a) Cyclic voltammeter.

b) Electrochemical impedance spectroscopy.

c) Galvanostatic charge- discharge.

d) Electrochemical hydrogen evolution reaction.

e) Oxygen evolution reaction.

f) Supercapacitor performance

5) Problem undertaken

The wide applications of nanostructured are based on the progress in the synthesis of new nanostructured materials of different sizes and new morphologies. And also for the following Spinel and or Perovskite will be study as:

1) Synthesis of various Spinel and or Perovskite materials
2) Their physical Characterization like structure, composition, surface appearance, optical studies etc.
3) Measurement of supercapacitor properties like CV, CCB, life time, impedance spectroscopy, measuring specific capacitance.
4) Based on obtained results manuscript in reported international journal will be published

5) References

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